



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification⁵ : H01B 1/24, C08K 3/04	A1	(11) International Publication Number: WO 94/24678 (43) International Publication Date: 27 October 1994 (27.10.94)
(21) International Application Number: PCT/GB94/00816 (22) International Filing Date: 18 April 1994 (18.04.94) (30) Priority Data: 9308062.0 16 April 1993 (16.04.93) GB (71)(72) Applicant and Inventor: ROMANIEC, Kazimierz, Czeslaw [GB/GB]; 57 Willis Street, Warrington, Cheshire WA1 3QE (GB). (74) Agents: McCALLUM, William, Potter et al.; Cruikshank & Fairweather, 19 Royal Exchange Square, Glasgow G1 3AE (GB).		(81) Designated States: AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, KZ, LK, LU, LV, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>With amended claims.</i>
(54) Title: METHOD OF PRODUCING AN ELECTRICALLY CONDUCTIVE MATERIAL		
(57) Abstract		
<p>A method of producing an electrically conductive material, comprises the steps: providing a non-aqueous solvent; dissolving a settable matrix-forming material in the solvent to form a non-aqueous solution; mixing particulate conductive material with the solution; applying the conductive material-containing solution to a carrier; and removing the solvent from the solution and permitting the matrix-forming material to set to form an electrically conductive composite.</p>		

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METHOD OF PRODUCING AN ELECTRICALLY CONDUCTIVE MATERIAL

This invention relates to a method of producing an electrically conductive material, and in particular to a method of producing an electrically conductive composite. The invention also relates to an electrically conductive composite.

It is known, for example from GB-A-2191668 and GB-A-2173200, to produce electrically conductive composites comprising electrically insulating polymers and carbon materials. GB-A-2173200 discloses a conductive material comprising carbon particles dispersed in a polymer, such as polyacrylonitrile or polyurethane. The document describes a method of producing a conductive fabric, in which polyamide fabric is coated with an aqueous solution of an aliphatic polymer containing carbon particles. The coated fabric is heated to evaporate the water. It has been found that the resulting composite may retain moisture from the manufacturing process (particularly when steam heating techniques are utilised as disclosed in GB 2 191 668), and may subsequently absorb moisture from the atmosphere. This results in a number of problems including varying the electrical characteristics of the composite, accelerating deterioration of surrounding materials, including metallic connections, and can encourage the growth of fungi and the like on the composite.

It is among the objects of the present invention to provide a method of producing an electrically conductive material which obviates or mitigates these disadvantages.

According to the present invention there is provided a method of producing an electrically conductive material, the method comprising:

providing a non-aqueous solvent;

dissolving a settable matrix-forming material in the

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solvent to form a non-aqueous solution;

mixing particulate conductive material with said solution;

applying the conductive material-containing solution to a carrier; and

removing the solvent from the solution and permitting the matrix-forming material to set to form an electrically conductive composite.

According to another aspect of the present invention there is provided a conductive composite material comprising a non-aqueous based polymer matrix and a particulate conductive material dispersed therethrough.

The material produced is substantially moisture free and will not tend to absorb moisture during use. This is particularly important in applications where the material is to be used in close proximity to a human or animal body and will therefore be exposed to perspiration which would otherwise be absorbed by the material and alter its electrical characteristics, encourage growth of fungi, and accelerate deterioration of the material and surrounding materials.

The material has particular application in forming heating elements, which may be used in heated vehicle seats, therapeutic heating pads, heated under-blankets and the like.

Preferably, the settable material is a monomer or polymer which is polymerised or cured after application to the carrier material. Most preferably, the settable material is an aliphatic compound.

Preferably also, the conductive material is carbon. The carbon may form 25 to 60% by weight of the total solid content of the solution, and most preferably forms 45% by weight of the total solid content of the solution.

Preferably also, a flammability inhibitor is incorporated in the composite. The flammability inhibitor may form up to 30% by weight of the total solid content of

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the solution, and most preferably forms 20% by weight of the total solid solution.

The carrier material may be separated from the set composite if it is desired to produce a conductive composite film. In such applications the carrier may be in the form of a silicone coated polymer sheet. Alternatively, the carrier material may be retained to form a support for the composite and may be in the form of a fabric or a continuous sheet. It is preferred that the film is perforated such that, in use, heat generated on the side of the sheet opposite the area to be heated may be more readily dispersed. Perforation also provides breathability, for greater comfort when the material is used, for example, as a heating pad in a vehicle seat.

Such films may be combined in a laminate, a preferred laminate comprising two films of the composite material with a scrim located therebetween. Preferably, the composite material is utilised as an adhesive, that is a layer of conductive-material containing solution is provided between the scrim and each film. Preferably also, the scrim carries conductors which form electrodes in the laminate. Preferably, the conductors are in the form of copper tinsel.

According to another aspect of the present invention there is provided an electrically conductive composite comprising an electrically conductive particulate material held in a non-conductive carrier, the composite being in the form of a perforated sheet.

These and other aspects of the invention will now be described, by way of example, with reference to the accompanying drawing which is a somewhat schematic view of laminate in accordance with one embodiment of the present invention.

The illustrated embodiment of the invention is in the form of a laminate 10 comprising a scrim 12 supporting films 14, 16 of an electrically conductive composite, and

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which laminate 10 may be utilised as a heating element in many applications, including a therapeutic heating pad, a domestic under-blanket, a heated pad for vehicle seats or as a wrapping for heated pipes. The laminate will be encased in a suitable insulating material (not shown) and connected to a thermostat controlled electrical supply 18 typically a 12 or 24 volts supply. Conductors 20 are provided through the scrim 12 to form electrodes, and in the illustrated embodiment the electrodes 20 are in the form of copper tinsel, that is thread provided with a wrapping of copper foil.

The films 14, 16 comprise a non-aqueous based polymer carrier having particulate carbon dispersed therethrough. The films 14, 16 are separately formed from a solution of a non-aqueous solvent, containing matrix-forming material and pH compatible carbon particles, which has been applied to a release sheet, the solvent evaporated and the matrix-forming material cured. To adhere the scrim 12 and films 14, 16 together the scrim 12 is coated on both sides with the carbon-containing solution.

EXAMPLE

A non-aqueous solvent in the form of a 1.5:1(w/w) mixture of isopropyl alcohol and toluene is provided. Aliphatic based polymer pellets as sold under the TRIXENE H35 trademark by Bayer are dissolved in the solvent to produce a clear, colourless liquid. Carbon particles, as sold under the Vulcan XC72R or CORAX trademark and having been milled to provide an average particle size of 10 microns, are then added to the solution, together with a flammability inhibitor, in the form of antimony trioxide. The carbon accounts for 45% by weight of the total solid content (that is including the dissolved polymer and flammability inhibitor) of the solution, the polymer pellets 35%, and flammability inhibitor accounts for 20%.

The solution is mixed to uniformly disperse the solid

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materials in the solution and is then applied to one side of a suitable casting film formed of silicone coated polyester. The solution may be applied by various methods as will be well known to those of skill in the art, including the method described in GB-A-2173200. The coated material is then heated to evaporate the solvent and cure the polymer material. The resulting film is perforated with 1 mm holes at 1 cm centres.

A 0.08 mm thick film formed using the components described above and method described in GB-A-2173200 has been found to possess the following mechanical properties.

Tensile Strength	Longitudinal	Lateral
	7.5 Kg/cm ²	6.5 Kg/cm ²
Elongation at break	Average 150%	
Embrittlement	-40 - -45 °C	
Loss of flexibility	-35 °C	
Hardness (Shore A)	88	

The film may be combined in a heating laminate as described above, and where the potential applied to the laminate is 12 Volts, spacing the conductors by around 5 cm (2 inches) results in the laminate being heated to approximately 50°C.

The resulting conductive composite is highly cross-linked and goes irreversibly solid upon curing. In addition, the composite is formed in the absence of water and is not easily wettable such that it is most unlikely that fungi and the like will be able to grow on the composite. The conductive material has also been found to have advantageous electrical properties including: the resistance\heating characteristics of the composite are self-limiting, such that the composite is most unlikely to overheat; and there is no build-up of static on the exterior of the laminate when encased in insulating material. It has also been found that heating provided by

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the composite is fairly constant between the electrodes and that the film forms a square law circuit. The use of aliphatic polymers as a carrier medium also offers advantages in that the manner in which the carbon particles are held in the carrier does not have an adverse effect on the conductive properties of the material, in contrast to, for example, a latex carrier. Further, it has been found that, due to the "excitation state" of the carbon, there is a relatively high heat energy distribution over frequencies extending into the far infra-red frequencies. Thus, the invention is useful in providing heating pads for therapeutic applications. The mechanical properties of the material have also been found to be good, providing resistance to abrasion, corrosion and moisture.

It will be clear to those of skill in the art that the above description is merely exemplary of the present invention and that various modifications and improvements may be made thereto without departing from the scope of the invention.

CLAIMS

1. A method of producing an electrically conductive material, the method comprising:
 - providing a non-aqueous solvent;
 - dissolving a settable matrix-forming material in the solvent to form a non-aqueous solution;
 - mixing particulate conductive material with said solution;
 - applying the conductive material-containing solution to a carrier; and
 - removing the solvent from the solution and permitting the matrix-forming material to set to form an electrically conductive composite.
2. The method of claim 1 wherein the settable material is a monomer or polymer which is polymerised or cured after application to the carrier material.
3. The method of claim 2 wherein the settable material is an aliphatic compound.
4. The method of claim 1, 2 or 3 wherein the conductive material is carbon.
5. The method of claim 4 wherein the carbon forms 25 to 60% by weight of the total solid content of the solution.
6. The method of claim 5 wherein the carbon forms 45% by weight of the total solid content of the solution.
6. The method of any one of the preceding claims wherein a flammability inhibitor is incorporated in the composite.
7. The method of claim 6 wherein the flammability

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inhibitor forms up to 30% by weight of the total solid content of the solution.

8. The method of claim 7 wherein the flammability inhibitor forms 20% by weight of the total solid solution.

9. The method of any one of the preceding claims wherein the carrier material is separated from the set composite to produce a conductive composite film.

10. The method of claim 9 wherein the carrier is in the form of a silicone coated polymer sheet.

11. The method of any one claims 1 to 8 wherein the carrier material is retained to form a support for the composite.

12. The method of any one of the preceding claims wherein the set composite is perforated.

13. The method of any one of the preceding claims wherein two set composite films are combined in a laminate comprising two films of the composite material with a scrim located therebetween.

14. The method of claim 13 wherein composite material is utilised as an adhesive and a layer of conductive-material containing solution is provided between the scrim and each film.

15. The method of claim 13 or 14 wherein the scrim carries conductors which form electrodes in the laminate.

16. A conductive composite material comprising a non-aqueous based polymer matrix and a particulate conductive material dispersed therethrough.

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17. An electrically conductive composite comprising an electrically conductive particulate material held in a non-conductive carrier, the composite being in the form of a perforated sheet.

AMENDED CLAIMS

[received by the International Bureau on 7 September 1994 (07.09.94);
original claims 1-17 replaced by amended claims 1-14 (2 pages)]

1. A method of producing an electrically conductive material, the method comprising:
 - providing a non-aqueous solvent;
 - dissolving a settable aliphatic monomer or polymer based matrix-forming material in the solvent to form a non-aqueous solution;
 - mixing particulate carbon with said solution;
 - applying the carbon-containing solution to a carrier;
 - and
 - removing the solvent from the solution and polymerising or curing the matrix-forming material to form an electrically conductive composite.
2. The method of claim 1 wherein the carbon forms 25 to 60% by weight of the total solid content of the solution.
3. The method of claim 2 wherein the carbon forms 45% by weight of the total solid content of the solution.
4. The method of any one of the preceding claims wherein a flammability inhibitor is incorporated in the composite.
5. The method of claim 4 wherein the flammability inhibitor forms up to 30% by weight of the total solid content of the solution.
6. The method of claim 5 wherein the flammability inhibitor forms 20% by weight of the total solid content of the solution.
7. The method of any one of the preceding claims wherein the carrier material is separated from the set composite to produce a conductive composite film.

8. The method of claim 7 wherein the carrier is in the form of a silicone coated polymer sheet.

9. The method of any one claims 1 to 6 wherein the carrier material is retained to form a support for the composite.

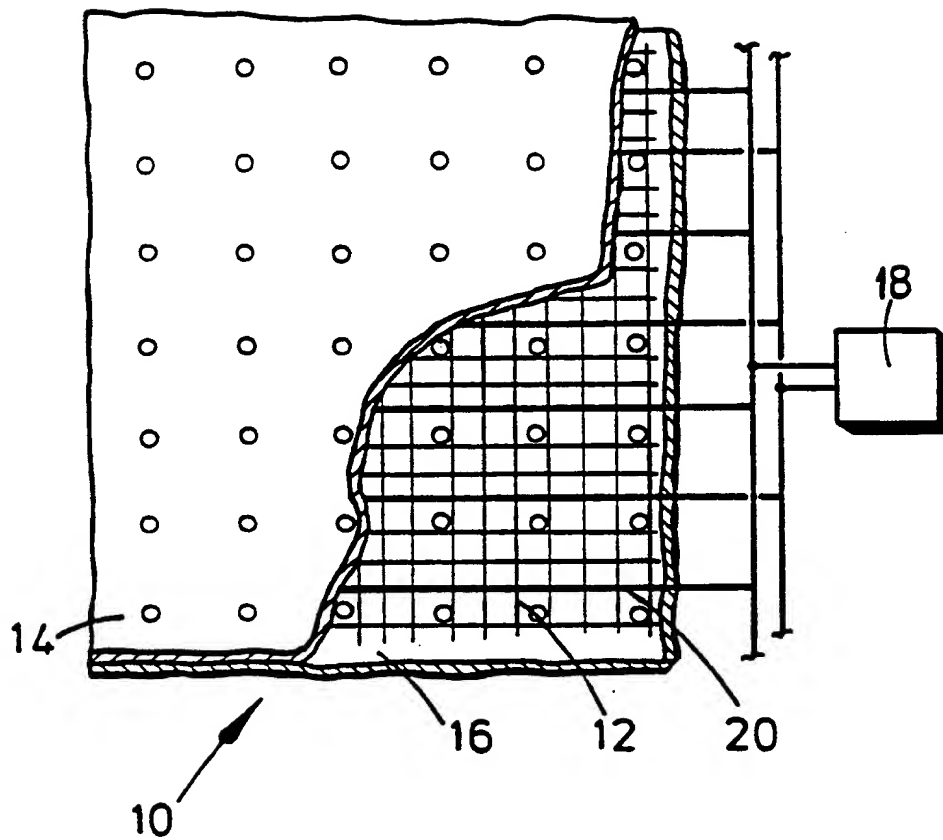
10. The method of any one of the preceding claims wherein the set composite is perforated.

11. The method of any one of the preceding claims wherein two set composite films are combined in a laminate comprising two films of the composite material with a scrim located therebetween.

12. The method of claim 11 wherein said composite material is utilised as an adhesive, a layer of conductive-material containing solution being provided between the scrim and each film.

13. The method of claim 11 or 12 wherein the scrim carries conductors which form electrodes in the laminate.

14. A conductive composite material comprising a non-aqueous based aliphatic polymer matrix with particulate carbon dispersed therethrough.

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SUBSTITUTE SHEET (RULE 26)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/GB 94/00816

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 H01B1/24 C08K3/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 H01B C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	US,A,5 151 222 (J.M.RUFFONI) 29 September 1992 see the whole document ---	1-6, 12, 13, 17, 18
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X	US,A,5 049 313 (R.L.FRENTZEL) 17 September 1991 see the whole document ---	1, 2, 4-6, 17
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Date of the actual completion of the international search

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

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